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DIFFUSION-CONTROLLED CURRENT AT THE STATIONARY FINITE DISK ELEC--ETC(U)
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9 Technical Report #2	2. GOVT ACCESSION NO. AD-A091 931	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 Diffusion-controlled Current at the Stationary Finite Disk Electrode. Theory.		5. TYPE OF REPORT & PERIOD COVERED 14 TR-2
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 Koichi Aoki [redacted] Janet Osteryoung		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-79-C-0644
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry State University of New York at Buffalo		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 43
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research/Chemistry Program Arlington, VA 22217		12. REPORT DATE 11 Oct[redacted]980
		13. NUMBER OF PAGES 33
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) LEVEL III A08906		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release: Distribution Unlimited

DTIC ELECTE NOV 1 8 1980 S C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for Publication in Journal of Electroanalytical Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

diffusion-controlled currents; finite disk electrode

sq.rt (Dt/a)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Contract N00014-79-C-0644

Task No. NR 056-722

TECHNICAL REPORT NO. 2

Diffusion-Controlled Current at the Stationary Finite Disk Electrode. Theory

by

Koichi Aoki and Janet Osteryoung

Prepared for Publication

in the

Journal of Electroanalytical Chemistry

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York

October, 1980

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ABSTRACT

Rigorous expressions for diffusion-controlled currents at a stationary finite disk electrode are derived through use of the Winer-Hofp technique. The chronoamperometric curve obtained varies smoothly from a curve represented by the Cottrell equation to a steady state value similar to that obtained for a spherical electrode as time elapses. The solution can be expressed also as the Cottrell term multiplied by a power series in the parameter $\sqrt{Dt}/a$, where a is the electrode radius. The present work is discussed in terms of the coefficient of the first term in this formulation.

INTRODUCTION

Most studies of mass transfer in electrochemical problems have focused on linear diffusion to and from a planar electrode or on diffusion in the radial direction at a spherical or a cylindrical electrode. In other words, diffusion is considered only in the direction perpendicular to an electrode, though the electrodes employed in practice have their own more complex geometries. Real electrode processes are frequently complicated by diffusion with directional components other than normal to the electrode, i.e., non-linear diffusion, especially near the edges of the electrode. We can take as examples of complicated diffusion shielding effects at the DME or the HMDE by the glass tip supporting the mercury drop [1-3], edge effects at planar electrodes [4-15] and effects of partially blocked electrodes [16-24]. These effects are strongly dependent not only on geometries of electrodes but also on the relation between dimensions of electrodes and the time scale of the experiment.

One of the simplest geometries of electrodes that complicates diffusion is a planar disk electrode embedded flush in an infinite insulating plane. Chronoamperometric curves at this electrode are expected to have the following behavior as time elapses: at sufficiently short times they should obey the Cottrell equation ($i \sim 1/\sqrt{t}$), be gradually influenced by three dimensional diffusion near edges of the electrode at longer times, and finally approach a steady state current, as is observed at a spherical electrode [25]. One of the interesting points of the stationary disk electrode is that the steady state current can be observed at long times though the electrode is stationary as well as planar. Another interesting point is that planar disk electrodes can be constructed easily to conform closely to a given model. This is in contrast to hanging mercury drop electrodes or shielded planar electrodes. The other fascinating point is that for proper dimensions and times such electrodes make it possible to determine n and D simultaneously from a single chronoamperogram [9,10,28,29].

Both theoretical and experimental work has been carried out on mass transport at the stationary disk electrode. Bard [4] concluded from potentiometric measurements that a planar disk electrode has a transition time which is similar to that obtained at a spherical electrode when the time scale is long enough. Lingane [5] gave a quantitative experimental description of the chronopotentiometric and chronoamperometric constants at unshielded planar disk electrodes. Soos and Lingane [6] derived an analytical expression for diffusion-limited currents at a planar disk electrode. However, their equation is just the sum of the Cottrell equation and the expression for the steady state current, so that it does not describe actual chronoamperometric curves. Flanagan and Marcoux [7] evaluated departure of chronoamperometric curves from the Cottrell term by means of digital simulation. Ito et al. [8] introduced an empirical parameter into an expression for the diffusion current as a result of chronoamperometric experiments at platinum microelectrodes. Kakihana et al. [9,10] did potentiostatic experiments at unshielded small disk electrodes in order to obtain more accurate values of diffusion coefficients of electroactive species. They also employed digital simulation using a corrected version of the scheme of Flanagan and Marcoux [7] and compared their simulated values with their experimental ones. Recently Sarangapani and DeLevie [11] challenged theoretically the problem of ac response at this kind of electrode;

their expression does not satisfy the boundary condition given. Dayton et al. [12] measured almost time independent diffusion current at small sizes of carbon fiber electrodes.

Most recently Oldham has analyzed theoretically the problem of current distribution for an infinitesimally thick electrode bounded in only one of the remaining four directions [14]. The solution can be applied through appropriate transformation to finite disk electrodes of moderate size. In addition, Heinze has developed a digital simulation model for current at a planar disk electrode [15].

Theoretical studies of complicated diffusion have been done on assumptions that potential theory valid only for the steady state may be applicable to time dependent systems [17-21], and non-linear parts of diffusion may be represented as mean concentrations [22-24]. Neither technique is a direct approach to non-linear diffusion. In the field of heat transfer, which is similar to the electrochemical problem from the phenomenological point of view, a rigorous solution has been given to systems with intricate geometrical boundaries [26] by employing the Wiener-Hopf method [27]. This technique is not only powerful but also applicable to many electrochemical problems concerning complicated diffusion with various kinds of geometries of electrodes.

The purpose of this paper is to derive rigorous expressions for diffusion-controlled currents at the unshielded planar disk electrode in quiescent solution.

DERIVATION

Let us consider a simple, reversible electrode reaction, $O + ne \rightleftarrows R$, involving only species soluble in the solution. We assume that diffusion coefficients of both species have the common value, D, and that migration can be neglected. Under these conditions, the expressions for diffusion-controlled currents at the planar disk electrode are derived for large values of t and for small values of t.

Large Values of t (Descending Series). The diffusion equation represented in polar coordinates is of the form

$$\frac{\partial C_j}{\partial t} = D \{\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C_j}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial C_j}{\partial \theta})\} \quad (j = O \text{ or } R) \tag{1}$$

where $C_j = C_j(r, \theta, t)$ is the concentration of species j, r is the distance from the center of the electrode and θ is the angle which the radius vector makes with the z-axis as shown in Fig. 1.

The initial conditions are given by

$$C_O(r, \theta, 0) = C^O, \; C_R(r, \theta, 0) = 0 \tag{2}$$

where C^O is the bulk concentration of species O. Taking into account that the Nernst equation holds at the electrode, we have the boundary condition for $\theta = \pi/2$

$$C_O(r, \pi/2, t) = \zeta C_R(r, \pi/2, t) \text{ for } 0 \leqq r \leqq a \tag{3}$$

where $\zeta = \exp[(nF/RT)(E - E_0)]$ and a is the radius of the electrode. Since the sum of the fluxes for the two species at the electrode is equal to zero, it follows that

$$\partial C_O(r, \pi/2, t)/\partial\theta + \partial C_R(r, \pi/2, t)/\partial\theta = 0 \text{ for } 0 \leqq r \leqq a \tag{4}$$

The boundary conditions at the insulating plane are given by

$$\partial C_j (r, \pi/2, t)/\partial\theta = 0 \text{ for } r > a \; (j = O \text{ or } R) \tag{5}$$

If $\sqrt{r}\,(C_O - C^O \zeta C_R)$ is replaced by v and the Laplace transformation is carried out with respect to t, eqns. (1), (2), (3) and (5) are reduced to

$$(r^2 s/D + 1/4)\, \bar{v} = r\partial\, (r\partial\bar{v}/\partial r)/\partial r + (1/\sin\theta)\partial(\sin\theta\partial\bar{v}/\partial\theta)/\partial\theta \tag{6}$$

$$\bar{v}(r, \pi/2) = \frac{C^0}{s}\sqrt{r} \text{ for } 0 \leq r \leq a$$
$$\partial\bar{v}(r, \pi/2)/\partial\theta = 0 \text{ for } r > a \tag{7}$$

where $\bar{v}$ means the Laplace transform of v. If we apply the Kontorovich-Lebedev transformation [30] given by

$$\phi(\mu,\theta) = \int_0^\infty \bar{v}(r,\theta)K_\mu (r\sqrt{s/D})(1/r)dr \tag{8}$$

to eqn. (6), taking into account $\bar{v} \to 0 (\sqrt{r})$ as $r \to 0$, we have

$$(\mu^2-1/4)\phi + (1/\sin\theta)(\partial(\sin\theta\partial\phi/\partial\theta)/\partial\theta) = 0 \tag{9}$$

Although eqn. (9) holds only for $|\mathrm{Re}\ \mu| < 1/2$, analytical continuation [31] makes it valid for any values of μ. The solution of eqn. (9) is

$$\phi(\mu,\theta) = B_1\ P_{\mu-1/2}(\cos\theta) + B_2\ Q_{\mu-1/2}(\cos\theta)$$

where P and Q are the first and the second kind Legendre functions [32], respectively, and B_1 and B_2 are any constants independent of θ. Since ϕ should be continuous at $\theta = 0$, B_2 is found to be zero. Eliminating B_1 in terms of the combination of ϕ and $\partial\phi/\partial\theta$ and letting θ be $\pi/2$ yields

$$P'_{\mu-1/2}(0)\phi(\mu,\pi/2) + P_{\mu-1/2}(0)\phi'(\mu,\pi/2) = 0 \tag{10}$$

where the prime means the derivative with respect to θ.

By considering eqns. (7) and (8), an alternative expression for eqn. (10) is written as

$$-(C^0/s)\int_0^a K_\mu(r\sqrt{s/D})\,(1/\sqrt{r})dr + \int_a^\infty \bar{v}(r,\pi/2)\,K_\mu(r\sqrt{s/D})(1/r)dr$$

$$= L(\mu)\int_0^a \bar{v}'\,(r,\pi/2)\,K_\mu(r\sqrt{s/D})(1/r)dr \qquad (11)$$

with

$$L(\mu) = -P_{\mu-1/2}(0)/P'_{\mu-1/2}(0) =$$

$$\Gamma(1/4+\mu/2)\Gamma(1/4-\mu/2)/\{2\Gamma(3/4+\mu/2)\Gamma(3/4-\mu/2)\} \qquad (12)$$

Now, a new function Φ is defined as

$$\Phi(\mu) = \Gamma(1+\mu)\xi^{-\mu}\int_0^a \bar{v}'(r,\pi/2)\,I_\mu\,(r\sqrt{s/D})\,(1/r)dr \qquad (13)$$

where $\xi = (a/2)\sqrt{s/D}$ and I_μ is the modified Bessel function of the first kind. $\Phi(\mu)$ is found to be regular in the region Re $\mu > -1/2$, because $I_\mu(z)$ becomes $(z/2)^\mu/\Gamma(1+\mu)$ [32] as μ approaches infinity, and $\bar{v}'$ has the order of $\sqrt{r}$ as r approaches zero. On making use of eqn. (A-2) in Appendix 1, the integral on the right hand side of eqn. (11) can be expressed in terms of Φ as

$$\int_0^a \bar{v}'\,(r,\tfrac{\pi}{2})\,K_\mu\,(\sqrt{\tfrac{s}{D}}\,r)\,\frac{dr}{r} = (1/2)\xi^{-\mu}\Gamma(\mu)\Phi(-\mu) + (1/2)\xi^{\mu}\Gamma(-\mu)\,\Phi(\mu) \qquad (14)$$

$L(\mu)$ defined by eqn. (12) can be decomposed into the product of two functions:

$$L(\mu) = L_p(\mu)/L_N(\mu) \qquad (15)$$

where

$$L_P(\mu) = \Gamma(1/4 + \mu/2)/2\Gamma(3/4 + \mu/2)$$

$$L_N(\mu) = \Gamma(3/4 - \mu/2)/\Gamma(1/4 - \mu/2)$$

$L_P(\mu)$ and $L_N(\mu)$ are analytic and non-zero in the regions Re $\mu > -1/2$ and Re $\mu < 1/2$, respectively. Substituting eqns. (14) and (15) into eqn. (11) and multiplying both sides by $L_N(\mu)/\xi^{\mu}\Gamma(-\mu)$ yields

$$V + X = W + (1/2)\, L_P(\mu)\, \Phi(\mu) \tag{16}$$

$$V(\mu) = (L_N(\mu)/\xi^{\mu}\Gamma(-\mu)) \int_0^a (-C^0/s) K_\mu\, (r\sqrt{s/D})(1/\sqrt{r})\, dr \tag{17}$$

$$X(\mu) = (L_N(\mu)/\xi^{\mu}\Gamma(-\mu)) \int_a^\infty \bar{v}\, (r,\pi/2)\, K_\mu(r\sqrt{s/D})(1/r)dr \tag{18}$$

$$W(\mu) = L_P(\mu)\Gamma(\mu)\Phi(-\mu)/2\xi^{2\mu}\Gamma(-\mu) \tag{19}$$

Since two unknowns, $\bar{v}(r,\pi/2)$ and $\bar{v}'(r,\pi/2)$ are involved in eqn. (16), explicit solutions cannot be obtained in an ordinary algebraic manner. However, the Wiener-Hopf technique [27] sometimes enables us to divide one equation into two independent ones leading to solutions. If we apply Cauchy's integral theorem [31] to $V(\mu)$ for $-1/2 < \text{Re}\,\mu < 0$ and take the imaginary part of the path of integration to infinity, we have

$$V(\mu) = V_P(\mu) + V_N(\mu) \tag{20}$$

$$\left.\begin{aligned} V_P(\mu) &= -(1/2\pi i) \int_{\beta-i\infty}^{\beta+i\infty} V(z)(z-\mu)^{-1}dz \\ V_N(\mu) &= (1/2\pi i) \int_{\beta'-i\infty}^{\beta'+i\infty} V(z)(z-\mu)^{-1}dz \end{aligned}\right\} \tag{21}$$

where $-1/2 < \beta < \mathrm{Re}\,\mu < \beta' < 0$. Inserting the ascending series of K_μ [33] into the integrand of eqn. (17) and integrating term by term results in

$$\int_0^a K_\mu\,(r\sqrt{s/D})(1/\sqrt{r})dr = (\pi\,\sqrt{a}/2\sin\mu\pi)\sum_{n=0}^{\infty}\,(1/n!)\cdot$$
$$\{\xi^{2n-\mu}/\Gamma(n-\mu+1)(2n-\mu+1/2) - \xi^{2n+\mu}/\Gamma(n+\mu+1)(2n+\mu+1/2)\} \qquad (22)$$

which is convergent for $|\mathrm{Re}\,\mu| < 1/2$. On extending the range of μ to all the complex values by analytic continuation, substituting eqns. (22) and (17) into eqn. (21) and shifting the path of integration to the left, simple poles occur at $z = -2n -1/2$ $(n = 0, 1, 2, \ldots)$ with residues $(-1)^n\,\xi^{2n}/\,\{(2n + \mu + 1/2)\,\Gamma(2n + 1/2)\}$. There are no poles at $z = j$, $(j = 1,2,\ldots)$ because of the relation

$$\sum_{n=0}^{\infty}\sum_{j=1}^{\infty}\,(1/n!)\,\{\xi^{2n+j}/\Gamma(n+j+1)(2n+j+1/2) - \xi^{2n-j}/\Gamma(n-j+1)(2n-j+1/2)\}$$
$$= 0 \qquad (23)$$

Hence V_p becomes

$$V_p = -(C^0\,\sqrt{a}/2s)\sum_{n=0}^{\infty}\,(-1)^n\,\xi^{2n}/\Gamma(2n+1/2)(2n+\mu+1/2) \qquad (24)$$

The function W can be expressed as a sum of W_p and W_N in a similar way. If eqn. (19) is substituted into eqn. (21) with W and W_p replacing V and V_p, respectively, and the path of integration is shifted to the left, simple poles arise from $\Gamma(1/4 + z/2)$ at $z = -2n-1/2$ $(n = 0,1,2,\ldots)$ with residues $(-1)^n/n!$ and from $\Gamma(z)$ at $z = -j$ $(j = 1,2,\ldots)$ with residues $(-1)^j/j!$. Consequently

$$W_P = -\sum_{n=0}^{\infty} \Gamma(n+1/2)\,\Phi(2n+1/2)\xi^{4n+1}/4n!\,\Gamma(2n+1/2)\Gamma(2n+3/2)(2n+\mu+1/2)$$

$$+\sum_{j=1}^{\infty} \Gamma(j/2+1/4)\,\Phi(j)\xi^{2j}/4(j-1)!\,j!\,\Gamma(j/2+3/4)(j+\mu) \qquad (25)$$

Although the integral part of eqn. (18) is analytic for all values of μ, X is analytic in the restricted region Re $\mu < 1/2$, owing to $L_P(\mu)/\Gamma(-\mu)$.

Combining eqn. (20) and $W = W_P + W_N$ with eqn. (16) yields

$$V_N + X - W_N = -V_P + W_P + L_P\Phi/2 = G(\mu)$$

where we have represented both sides as $G(\mu)$. Since the left hand side and the middle are analytic at least in the regions Re $\mu < 0$ and Re $\mu > -1/2$, $G(\mu)$ is analytic in the strip $-1/2 <$ Re $\mu < 0$. However we can let G be analytic over the entire region of μ by analytic continuation. Since $\Phi = O(1/\mu)$, $L_P = O(1/\sqrt{\mu})$, $V_P = O(1/\mu)$ and $W_P = O(1/\mu)$ as μ approaches infinity, G becomes zero as μ approaches infinity. If Liouville's theorem [31] is applied to two kinds of features for G, G is found to be identically zero. Hence

$$\Phi(\mu) = 2(V_P - W_P)/L_P \qquad (26)$$

Inserting eqns. (24) and (25) into eqn. (26), we can readily express Φ as

$$\Phi(\mu) = -(C^0\sqrt{a}/\sqrt{\pi}sL_P)\sum_{n=0}^{\infty} a_n(\mu)\xi^n \qquad (27)$$

The functions a_n are functions of μ and can be successively determined to give

$$a_0(\mu) = 2/(2\mu+1)$$

$$a_1(\mu) = 4/\pi(2\mu+1)$$

$$a_2(\mu) = -8/3(2\mu+5) + 8/\pi^2(2\mu+1) - 2/3(\mu+1)$$

$$a_3(\mu) = 16(1/\pi^2 - 2/9)/\pi(2\mu+1) - 4/3\pi(\mu+1)$$

$$\vdots$$

The total current, noting eqn. (4), is given by

$$\begin{aligned}[\overline{I/nF}] &= -\int_0^a 2\pi D(\partial\overline{C}_0(r,\pi/2)/\partial\theta)dr \\ &= -((2\pi D)/(1+\zeta)) \int_0^a \overline{v}'(r,\pi/2)(1/\sqrt{r})dr \qquad (28)\end{aligned}$$

It is shown in Appendix 1 that the inverse transform of eqn. (13) is given by

$$\overline{v}'(r,\pi/2) = (1/\pi i) \int_{-i\infty}^{i\infty} (\Phi(\mu)\xi^{\mu}/\Gamma(\mu))K_{\mu}(r\sqrt{s/D})d\mu \qquad (29)$$

If we substitute eqn. (29) into eqn. (28), exchange the order of integration and carry out integration with respect to r, noting eqn. (22), we have

$$[\overline{I/nF}] = -(\pi^2 D\sqrt{a}/\pi i(1+\zeta)) \int_{-i\infty}^{i\infty} (\Phi(\mu)/\Gamma(\mu)\sin\mu\pi)\cdot$$
$$\sum_{n=0}^{\infty} (1/n!)\{\xi^{2n}/\Gamma(n-\mu+1)(2n-\mu+1/2) - \xi^{2n+\mu}/\Gamma(n+\mu+1)(2n+\mu+1/2)\}d\mu$$

Completing the path of integration in the right half plane and using eqn. (23), simple poles appear at $\mu = 2n+1/2$. When the residues are calculated and eqn. (27) is substituted into the resulting equation, it follows that

$$[\overline{I/nF}] = (4\sqrt{\pi}\, C^0 Da/s(1+\zeta)) \sum_{k=0}^{\infty} \sum_{n=0}^{[k/2]} (-1)^n \xi^k\, a_{k-2n}(2n+1/2)/\Gamma(2n+1/2)$$

where [k/2] means the integer part of k/2. The inverse Laplace transform is given by

$$I = (4nFC^0 Da/(1+\zeta))[1 + 2/\pi^{3/2}\sqrt{\tau} +$$

$$(1/\sqrt{\pi}) \sum_{k=1}^{\infty} \sum_{n=0}^{k} (-1)^{k+n}\, \Gamma(k+1/2)\, a_{2k-2n+1}(2n+1/2)\tau^{-k-1/2}/\Gamma(2n+1/2)]$$

$$= (4nFC^0 Da/(1+\zeta))\, [1 + 0.35917\, \tau^{-1/2} + 0.24648\, \tau^{-3/2} + 0.20648\, \tau^{-5/2} + \cdots] \qquad (30)$$

where $\tau = 4Dt/a^2$.

Small Values of t (Asymptotic Expansion). The diffusion equations in circular cylindrical coordinates are given by

$$\partial C_j/\partial t = D\, \{(1/r)\partial(r\partial C_j/\partial r)/\partial r + \partial^2 C_j/\partial z^2\}\ (j = 0 \text{ or } R) \qquad (31)$$

The initial and boundary conditions are the same as eqns. (2), (3), (4) and (5) if θ is altered to z and z is set to be zero. On making a change of variable, $v = \sqrt{r}\,(C_0 - C^0 - \xi C_R)$, and performing Laplace transformation, eqn. (31) becomes

$$s\bar{v}/D = (1/\sqrt{r})\partial[r\partial(\bar{v}/\sqrt{r})/\partial r]/\partial r + \partial^2\bar{v}/\partial z^2$$

Applying the Hanckel transformation of order zero [31], given by

$$U(p,z) = \int_0^{\infty} \bar{v}(r,z)\, \sqrt{rp}\;\; J_0(rp)dr \qquad (32)$$

to the above equation yields

$$d^2U/dz^2 = (p^2 + s/D)U$$

where the relation, $\bar{v} = O(\sqrt{r})$ as $r \to 0$, has been used. The solution of the differential equation is obviously given by $A \cdot \exp[-\sqrt{p^2 - s/D}\, z]$. When we eliminate a constant, A, from U(p,0) and dU(p,0)/dz, we have

$$\sqrt{p^2 + s/D}\ \ U(p,0) + dU(p,0)/dz = 0$$

If we rewrite this in the integral form with the aid of eqn. (32) as well as the boundary conditions and make use of the following expression [35]

$$\int_0^a r\, J_0(rp)dr = (a/p)\ J_1(ap) \tag{33}$$

then we obtain

$$-C^0 a\ J_1(ap)/s\sqrt{p} \ + \int_a^\infty \bar{v}(r,0)\ \sqrt{rp}\ J_0(rp)dr$$

$$+ M \int_0^a \bar{v}'(r,0)\ \sqrt{rp}\ J_0(rp)dr = 0 \tag{34}$$

where $M = M(p) = 1/\sqrt{p^2 + s/D}$ and $\bar{v}'(r,0) = \partial\bar{v}\ (r,0)/\partial z$.

We introduce three new functions:

$$U_+(p) = (1/2) \int_a^\infty \{\bar{v}(r,0)\ \sqrt{rp}\ H_0^{(1)}\ (rp)/H_1^{(1)}(ap)\ \sqrt{ap}\}dr \tag{35}$$

$$U_-(p) = (1/2) \int_a^\infty \{\bar{v}(r,0)\sqrt{rp}\ H_0^{(2)}(rp)/H_1^{(2)}(ap)\sqrt{ap}\}dr \tag{36}$$

$$U_0'(p) = \int_0^a \bar{v}'(r,0)\ \sqrt{rp}\ J_0(rp)dr \tag{37}$$

where $H_0^{(1)}$, $H_1^{(1)}$, $H_0^{(2)}$ and $H_1^{(2)}$ are Bessel functions of the third kind [36]. Inserting the asymptotic expansions of Bessel functions of the third kind into eqns. (35) and (36) and letting r be r+a leads to

$$U_{\pm}(p) \sim \pm (i/2) \int_0^\infty \bar{v}(r+a,0)\, e^{\pm ipr} dr \tag{38}$$

for large values of Re p.

It is well known that the concentration profile can be represented by the profile at a spherical electrode as r becomes large. Thus, $\bar{v}(r,0)$ has the order of $r^{-3/2}\exp[-\sqrt{s/D}\,(r-a)]$ [25]. If we substitute this into eqn. (38), we find $U_+(p)$ is analytic in Im $p > -$ Re $\sqrt{s/D}$ and $U_-(p)$ is analytic in Im $p <$ Re $\sqrt{s/D}$ according to the theory of Laplace transformation. Expressing eqn. (34) by eqns. (35), (36) and (37) through use of the relation $2J_\nu = H_\nu^{(1)} + H_\nu^{(2)}$, dividing the resulting equation by $H_1^{(1)}(ap)\sqrt{ap}\, e^{\pi i/4}(p + i\sqrt{s/D})^{-1/2}$, and rearranging it, we have

$$U_+/M_+ + U_0^{\wedge}M_-/H_1^{(1)}(ap)\sqrt{ap} + R + S = 0 \tag{39}$$

where

$$M_+ = M_+(p) = e^{\pi i/4}\,(p + i\,\sqrt{s/D})^{-1/2}$$

$$M_- = M_-(p) = e^{-\pi i/4}\,(p - i\,\sqrt{s/D})^{-1/2}$$

$$R = -C^0\sqrt{a}/2spM_+ \tag{40}$$

$$S = (U_- - C^0\sqrt{a}/2sp)H_1^{(2)}(ap)/M_+H_1^{(1)}(ap) \tag{41}$$

M_+ and M_- are analytic in the regions Im $p > -$Re $\sqrt{s/D}$ and Im $p <$ Re $\sqrt{s/D}$, respectively, and their product equals M.

For applying the Wiener-Hopf technique, R is expressed, according to Cauchy's integral theorem [31] as

$$R = R_+ + R_- \qquad (42)$$

$$R_+ = (1/2\pi i) \int_{-\infty+\beta i}^{\infty+\beta i} (R(z)/(z-p))dz$$

$$R_- = -(1/2\pi i) \int_{-\infty+\beta' i}^{\infty+\beta' i} (R(z)/(z-p))dz \qquad (43)$$

where $-\mathrm{Re}\sqrt{s/D} < \beta < \mathrm{Im}\, p < \beta' < 0$. By closing the path of the integral in eqn. (43) to the upper half plane and calculating the residue at $z = 0$, R_- becomes

$$R_- = -(C^0\sqrt{a}/2sp)(s/D)^{1/4}$$

Hence

$$R_+ = R - R_- = (C^0\sqrt{a}/2sp)\,\{(s/D)^{1/4} - 1/M_+\} \qquad (44)$$

S can be separated into two parts,

$$S = S_+ + S_- \qquad (45)$$

$$S_+ = (1/2\pi i) \int_{-\infty+\beta i}^{\infty+\beta i} \{U_-(z) - C^0\sqrt{a}/2sz\}\,[H_1^{(2)}(az)/H_1^{(1)}(az)M_+(z)(z-p)]dz \qquad (46)$$

where S_- corresponds to eqn. (43). Since $H_1^{(2)}(z)/H_1^{(1)}(z) \sim -ie^{-2iz}$, the singular point of the integrand in eqn. (46) is restricted only to $z = -i\sqrt{s/D}$ coming from M_+ in the lower half plane. The singularities in the bracket of eqn. (46) are located at $z = i\sqrt{s/D}$ and $z = 0$, both of which are pretty far from $z = -i\sqrt{s/D}$ for large values of $|s|$. Therefore it is possible to let z be $-i\sqrt{s/D}$ only in the bracket of eqn. (46) when the path of integration is shifted to the lower half plane. Changing the variable $z = -i\sqrt{s/D} + iw$, carrying out integration and employing the relation,

$$U_-(e^{-\pi i}p) = -U_+(p) \tag{47}$$

we have the following leading term:

$$S_+ \sim \{U_+(i\sqrt{s/D}) - C^0\sqrt{aD}/2is^{3/2}\}e^{-2a\sqrt{s/D}}/2^{5/2}\sqrt{\pi}a^{3/2}(i\sqrt{s/D} + p) \tag{48}$$

On combining eqn. (39) with eqns. (42) and (45),

$$R_+ + S_+ + U_+/M_+ = -U_0' M_-/H_1^{(1)}(ap)\sqrt{ap} - R_- - S_- \tag{49}$$

R_+ and S_+ as well as U_+/M_+ are analytic in the region of Im $p > -$Re $\sqrt{s/D}$, while each term on the right hand side is analytic in Im $P < 0$ because

$$U_0'/H_1^{(1)}(ap)\sqrt{ap} \sim (1/2) \int_0^a (ie^{i(r-a)p} - e^{-i(r+a)p})\ \bar{v}'(r,0)dr$$

Since all the terms on the left hand side of eqn. (49) tend to zero as $p \to i\infty$, it follows, according to Liouville's theorem [31],

$$U_+(p) = -M_+(p)\ \{R_+(p) + S_+(p)\} \tag{50}$$

Substituting eqns. (44) and (48) into eqn. (50) and letting p be $i\sqrt{s/D}$, we can see that $U_+(i\sqrt{s/D})$ has the order of $1/(sp)$. Therefore, S_+ has the order of $(1/s)\exp[-\sqrt{s}]$, which can be negligible for large values of $|s|$. Then, eqn. (50) becomes asymptotically

$$U_+(p) \sim (C^0\sqrt{a}/2sp)\ \{1-M_+(p)(s/D)^{1/4}\} \tag{51}$$

From the combination of eqn. (47) and (51), U_- is given by

$$U_-(p) \sim (C^0\sqrt{a}/2sp)\ \{1 - M_-(p)(s/D)^{1/4}\}$$

If U_+ and U_- are eliminated from eqn. (39) with eqns. (40) and (41), U'_0 takes the form

$$U'_0(p) \sim (C^0 a/2s\sqrt{p})(s/D)^{1/4}\ \{H_1^{(1)}(ap)/M_- + H_1^{(2)}(ap)/M_+\} \qquad (52)$$

The flux for the total current is given, in the Laplace transform, by

$$[\overline{I/nF}] = \int_0^a 2\pi rD\ (\partial\overline{C}_0(r,0)/\partial z)dr$$

$$= (2\pi D/(1+\zeta))\int_0^a \sqrt{r}\ \ \overline{v}'(r,0)dr$$

Substituting the Hanckel transform of U'(p,0), given by

$$\overline{v}'(r,0) = \int_0^\infty U'(p,0)\ \sqrt{rp}\ J_0(rp)dp$$

into the above equation, changing the order of integration and integrating with respect to r by use of eqn. (33), we have

$$[\overline{I/nF}] = (2\pi Da/(1+\zeta))\int_0^\infty (J_1(ap)U'(p,0)/\sqrt{p})dp$$

$U'(p,0)$ is equal to $U'_0(p)$ since $\overline{v}'(r,0)= 0$ for $r > a$ due to the boundary condition on the insulated wall.

Hence, replacing U' by U'_0 (given by eqn. (52)) leads to

$$[\overline{I/nF}] \sim (\pi C^0 Da^2 T/(1+\zeta)s)(s/D)^{1/4}$$

where

$$T = \int_0^\infty \{H_1^{(1)}(ap)/M_- + H_1^{(2)}(ap)/M_+\} (J_1(ap)/p)dp \tag{53}$$

The integral in eqn. (53) is evaluated in Appendix 2 to give

$$T = (s/D)^{1/4}\{1+(1/\sqrt{\pi}) \sum_{n=1}^{\infty} \Gamma\ (2n-3/2)\Gamma(n+1/2)^2\xi^{1-2n}/\Gamma(3/2-n)\Gamma(5/2-n)\Gamma(2n)^2\}$$

The inverse transform for the total current is

$$\begin{aligned} I \sim\ & (4nFC^0Da/(1+\zeta))\ \{\sqrt{\pi}/2\sqrt{\tau} \\ & + (\sqrt{\pi}/2) \sum_{n=1}^{\infty} \Gamma(2n-3/2)\Gamma(n+1/2)^2\tau^{n-1}/\Gamma(n)\Gamma(2n)^2\Gamma(3/2-n)\Gamma(5/2-n)\} \\ & = (4nFC^0Da/(1+\zeta))\{\sqrt{\pi}/2\sqrt{\tau} + \pi/4 - 3\pi\tau/2^{10} - 315\pi\tau^2/2^{21}\cdots\} \end{aligned} \tag{54}$$

DISCUSSION

The first term in eqn. (30) represents the solution for the steady state, derived from potential theory [37,38], while the leading term in eqn. (54) corresponds to the well-known Cottrell equation. They express satisfactorily the two kinds of limiting behaviors of i-t curves which are intuitively expected.

The function, f, given by

$$I = \{4nFC^0Da/(1+\zeta)\}\ \ f(\tau) \tag{55}$$

is calculated numerically from eqns. (30) and (54), and the values are plotted against τ in Fig. 2. The curve computed from eqn. (30) meets the curve evaluated from eqn. (54) in the domain $1.4 < \tau < 3.2$. This fact indicates that eqns. (30) and (54) suffice to describe chronoamperometric curves of real systems with good accuracy.

The contribution of the edge effect is revealed in the second and the subsequent terms of eqn. (54). The ratios of the edge contribution terms to currents due to the Cottrell term are less than 5%, 10% and 30% for the values of Dt/a^2 less than 8×10^{-4}, 3.2×10^{-3} and 2.9×10^{-2}, respectively. On the other hand, if values of Dt/a^2 are larger than 53, 3.5 and 0.65, the discrepancies from the steady state are within 5%, 10% and 30% of the steady state current, respectively.

Some studies on diffusion-controlled currents at a stationary disk electrode have been directed toward evaluation of the term succeeding the Cottrell term. According to Soos and Lingane [6], the current expression can be expanded in the form

$$I = \pi a^2 nFC^0 \sqrt{D/\pi t}\,\{1 + a_1\sqrt{Dt}/a + \cdots\} \tag{56}$$

where the coefficient a_1 is a constant to be determined. Some values of a_1 reported so far are listed in Table 1 together with the value calculated from eqn. (54). The latter value is very close to the simulated and experimental values which were obtained in many iterated runs by Kakihana et al. [9,10] and experimental values by Ito et al. [8].

Dimensionless i-t curves obtained analytically by Soos and Lingane [6] and computed with digital simulation by Kakihana et al. [9,10] are shown in Fig. 2. Since the expression by Soos and Lingane is just the sum of the Cottrell term and the steady state term, it does not obviously describe the real i-t curve. The simulated curve, C, is overlapped on curve A for small values of τ while it deviates from curve A as time elapses. This is a natural result if it is noted that digital simulation frequently involves errors for a number of iterations of computation corresponding to long electrolysis time. Most experimental chronoamperometric curves have been measured in the range $\tau < 0.3$ [9], in which they are in agreement with both simulated and our analytical curves within 3% error.

The clever analytical solution of Oldham [14] is stated to be accurate for $\tau < 0.16$. In fact it overestimates the value of $f(\tau)$ by only 0.7% for $\tau = 0.16$. The approximation remains reasonably accurate for larger values of τ. For example, for $\tau = 1$, where the solution of Soos and Lingane overestimates $f(\tau)$ by 24%, the corresponding error in Oldham's solution is only 2.8%.

Sarangapani and DeLevie derived an analytical expression for the ac response at a finite disk electrode [11]. However, eqn. (15) in their paper does not satisfy the boundary condition at $r \to \infty$. If we carry out the integration of their eqn. (19) in a fashion similar to that given in Appendix 2 and take the frequency to be zero, the result should be identical with eqn. (30) or (54). However, the two leading terms provide $I \sim -2.67\ nFC^0Da$ for the steady current and $I \sim -nFC^0a^2\sqrt{D}\ (\pi t)^{-1/2}$ for small values of t as a result of integrating and performing inverse Laplace transformation of their expression. Neither of these results are reasonable.

Table 1. Magnitude of the edge effect given by the coefficient of the first correction term to the Cottrell equation. The coefficient, a_1, is defined by eqn. (56).

Authors	Values of a_1	Methods	References
Lingane	2.12 ± 0.11	experimental	5
Soos and Lingane	$\frac{4}{\sqrt{\pi}} = 2.257....$	analytical	6
Flanagan and Marcoux	1.92 (published) 1.79 (corrected)	simulated	7 9,10
Kakihana et al.	$1.74 \sim 2.14$ $1.77 \sim 1.98$	experimental simulated	9
Dayton et al.	2.16 ± 0.35 (at carbon paste) 3.21 ± 0.27 (at carbon fiber)	experimental	12
Ito, Asakura and Nobe	1.77	experimental	8
Heinze	1.80-2.20	simulated	15
This work	$\sqrt{\pi} = 1.772...$	analytical	--

APPENDIX 1

This appendix shows that the inverse form of the transformation defined by eqn. (13) is given by eqn. (29). Let us prove that the right hand side of eqn. (29) in which Φ is replaced by eqn. (13), i.e.,

$$(1/\pi i) \int_{-i\infty}^{i\infty} \mu \int_0^a (\bar{v}' I_\mu(qt)/t)dt\ K_\mu(qr)d\mu = J \qquad \text{(A-1)}$$

is equal to $\bar{v}'$, where $q = \sqrt{s/D}$. Substituting the relation [33]

$$K_\mu(z) = (\pi/2\sin\mu\pi)\ \{I_{-\mu}(z) - I_\mu(z)\} \qquad \text{(A-2)}$$

into eqn. (A-1) yields

$$J = (1/\pi i) \int_{-i\infty}^{i\infty} \int_0^a (\pi\mu\bar{v}'/2t\sin\mu\pi)\ \{I_\mu(qt)I_{-\mu}(qr) - I_\mu(qt)I_\mu(qr)\}\cdot dtd\mu \qquad \text{(A-3)}$$

If μ is replaced by $-\mu$ in the first term of the bracket and eqn. (A-2) is employed for $I_{-\mu}(qt) - I_\mu(qt)$, eqn. (A-3) becomes

$$J = (1/\pi i) \int_{-i\infty}^{i\infty} \mu T(\mu)\ I_\mu(qr)d\mu \qquad \text{(A-4)}$$

where

$$T(\mu) = \int_0^a (\bar{v}'(r, \pi/2)\ K_\mu(qr)/r)dr \qquad \text{(A-5)}$$

Since $\bar{v}'$ vanishes for $r > a$, it is possible to extend the upper limit of the integral to infinity. Then T becomes the Kontorovich-Lebedev transform (see Eqn. 8) of $\bar{v}'(r, \pi/2)$. Eqn. (A-4) can be separated into the integrals from $-i\infty$ to 0 and from 0 to $i\infty$. Changing variables $\mu = ix$ in the former integral and $\mu = -ix$ in the latter gives

$$J = (i/\pi) \int_0^\infty x\, T(ix)\, \{I_{ix}(qx) - I_{-ix}(qx)\} dx$$

If eqn. (A-2) is inserted into the above equation, J is given by

$$J = (2/\pi^2) \int_0^\infty x \sinh(\pi x)\, T(ix) K_{ix}(qx) dx$$

This is the inverse Kontorovich-Lebedev transform [30] for eqn. (A-5).

Therefore, J is equal to $\overline{v}(r, \pi/2)$.

APPENDIX 2

In this appendix, the integral value expressed by eqn. (53) is evaluated. We introduce a function,

$$A = \int_0^\infty \{H_\nu^{(1)}(ap)/N_-(p) + H_\nu^{(2)}(ap)/N_+(p)\} (J_1(ap)/p)dp$$

where $N_+(p) = e^{\pi i/4} (p + i \sqrt{s/D})^q$, $N_-(p) = e^{-\pi i/4} (p - i\sqrt{s/D})^q$ and ν is any real constant. It is evident that A tends to eqn. (53) if ν and q approach 1 and -1/2, respectively. Expressing the Bessel functions of the third kind in A as a combination of Bessel functions of the first kind yields [36]

$$A = (1/i\sin\nu\pi) \int_0^\infty \{[J_{-\nu}(ap) - e^{-\nu\pi i} J_\nu(ap)]/N_-(p)$$
$$-[J_{-\nu}(ap) - e^{\nu\pi i} J_\nu(ap)]/N_+(p)\} (J_1(ap)/p)dp \qquad \text{(A-6)}$$

The integral representation of a product of Bessel functions is given by [39]

$$J_1(z)J_\nu(z) = (1/2\pi i) \int_{c-i\infty}^{c+i\infty} \{\Gamma(-x)\Gamma(2x+\nu+2)(z/2)^{2x+\nu+1}/\Gamma(x+\nu+1)$$
$$\Gamma(x+\nu+2)\Gamma(x+2)\}dx \qquad \text{(A-7)}$$

where $-\nu/2 - 1 < c < 0$.

Replacing the products of the Bessel functions in eqn. (A-6) by eqn. (A-7) and changing the order of integrals, we obtain

$$A = -(1/2\pi\sin\nu\pi) \int_{c'-i\infty}^{c'+i\infty} \{(f_2 - e^{-\nu\pi i} f_1) \int_0^\infty (p^{2x-\nu}/N_-(p))dp$$
$$-(f_2 - e^{\nu\pi i} f_1) \int_0^\infty (p^{2x-\nu}/N_+(p))dp\}(a/2)^{2x-\nu+1}dx \qquad \text{(A-8)}$$

where

$$f_1 = f_1(x,\nu) = \Gamma(-x+\nu)\ \Gamma(2x-\nu+2)/\Gamma(x+1)\Gamma(x+2)\Gamma(x-\nu+2)$$
$$f_2 = f_2(x,\nu) = \Gamma(-x)\Gamma(2x-\nu+2)/\Gamma(x-\nu+1)\Gamma(x-\nu+2)\Gamma(x+2)$$

We have set x to be $x-\nu$ in the integral representation for J_1J_ν in which the integrand is f_1. Therefore the path of the integral for f_2 is located in the left half plane while that for f_1 is to the left of x = 1. If we carry out the integration in eqn. (A-8) with respect to p, we have [40]

$$\int_0^\infty (p^{2x-\nu}/N_{\pm}(p))dp = e^{\pm(x-\nu/2-q/2+1/4)\pi i}\ (s/D)^{x-\nu/2-q/2+1/2}\cdot$$
$$\Gamma(2x-\nu+1)\Gamma(-2x+\nu+q-1)/\Gamma(q) \qquad \text{(A-9)}$$

Since these integrals are convergent for $q > 0$ and for $0 < \text{Re}\ x < \text{Re}\ (q/2)$, q is temporarily kept positive until integration is carried out with respect to x. After that, q will be extended to all real values by analytic continuation and then be set equal to $-1/2$.

Substituting eqn. (A-9) into eqn. (A-8) and rearranging it yields

$$A = (2(s/D)^{-q/2}/2\pi i\Gamma(q)\sin\nu\pi\int_{c'-i\infty}^{c'+i\infty} (a^2s/4D)^{x-\nu/2+1/2}\cdot$$
$$\Gamma(2x-\nu+1)\Gamma(-2x+\nu+q-1)\ \{f_2\sin(-x+\nu/2+q/2-1/4)\pi$$
$$-f_1\ \sin\ (-x-\nu/2+q/2-1/4)\pi\}dx$$

When we take the limit as $\nu \to 1$ by use of L'Hospital's theorem, we have

$$\lim_{\nu\to 1} A = -(2(s/D)^{-q/2}/2\pi^2 i\Gamma(q))\int_{c'-i\infty}^{c'+i\infty} (F_2(x)+F_1(x))dx \qquad \text{(A-10)}$$

$$F_1(x) = h_1(x)f_1(x,1)\ \{h_2(x)+\psi(1-x)-(\pi/2)\cot(-x+q/2+1/4)\pi\}$$

$$F_2(x) = h_1(x)f_2(x,1)\ \{h_2(x)+\psi(x)+(\pi/2)\cot(-x+q/2+1/4)\pi\}$$

$$h_1(x) = (a^2s/4D)^x\Gamma(2x)\Gamma(-2x+q)\sin(-x+q/2+1/4)\pi$$

$$h_2(x) = -(1/2)\ell n(a^2s/4D) - \psi(2x) + \psi(q-2x) - \psi(2x+1) + \psi(x+1)$$

where $\psi(x)$ is the Psi or Digamma function [41]. As described before, the path of integration in eqn. (A-10) is on the left of $c' = 1$ for F_1 and of $c' = 0$ for F_2. Since poles do not arise from $\Gamma(q-2x)$ or $\psi(q-2x)$ under the conditions of eqn. (A-9), poles resulting from closing the contour to the left half plane are the simple poles at $x = 0$ coming from three terms involved in the parenthesis of F_2 and double poles at $x = 1/2 - n$ ($n = 1,2,3,\cdots$) coming from $\Gamma(2x)\psi(2x+1)$. One should take notice that there is no pole at $x = -n$ ($n = 1,2,3,\cdots$).

Each contribution of simple poles at $x = 0$ can be calculated in the familiar method to give $-(1/2)(s/D)^{1/4}$, $(s/D)^{1/4}$ and $(1/2)(s/D)^{1/4}$ in turn, after taking the limit $q \to -1/2$. If we let the residue of eqn. (A-10) at $x = 0$ be A_0, we obtain

$$A_0 = (s/D)^{1/4}$$

In order to calculate the residue at $x = 1/2-n$, which is symbolized by A_n, we should evaluate $\partial[\{F_2(x)+F_1(x)\}(2x+2n-1)^2]/\partial x$ at $x = 1/2-n$. If the following relations:

$$\psi(1/2-n) = \psi(1/2+n)$$

and

$$[\partial(\psi(x) - \psi(1-x) + \pi\cot(-x+q/2+1/4)\pi)/\partial x]_{x=1/2-n} \to 2\pi^2 \quad (q \to -1/2)$$

are used for the calculation of the residue, A_n can readily be obtained

$$A_n = (1/\sqrt{\pi})(s/D)^{1/4}(a^2 s/4D)^{1/2-n}\Gamma(2n-3/2)\Gamma(n+1/2)^2/\Gamma(3/2-n)\cdot$$
$$\Gamma(5/2-n)\Gamma(2n)^2$$

The sum of A_n provides

$$T = \lim_{\substack{\nu \to 1 \\ q \to -1/2}} A = (s/D)^{1/4}\{1+(1/\sqrt{\pi}) \sum_{n=1}^{\infty} (a^2 s/4D)^{1/2-n}\, \Gamma(2n-3/2)\cdot$$
$$\Gamma(n+1/2)^2/\Gamma(3/2-n)\Gamma(5/2-n)\Gamma(2n)^2\}$$

FIGURE CAPTIONS

Fig. 1. Spherical and cylindrical coordinates located on the stationary micro disk electrode. Dashed vector for the cylindrical coordinate; solid vector for the spherical coordinate.

Fig. 2. Dimensionless chronoamperometric curves.

A: calculated from eqn. (54), B: calculated from eqn. (30), C: computed by means of digital simulation [9,10], D: curve by Soos and Lingane [6]. The ordinate is the function $f(\tau)$ given by eqn. (55).

ACKNOWLEDGEMENT

We would like to thank Dr. K. Tokuda and Dr. G. P. Sâto for giving us the data of the digital simulation and the experiments. This work was supported in part by the Office of Naval Research.

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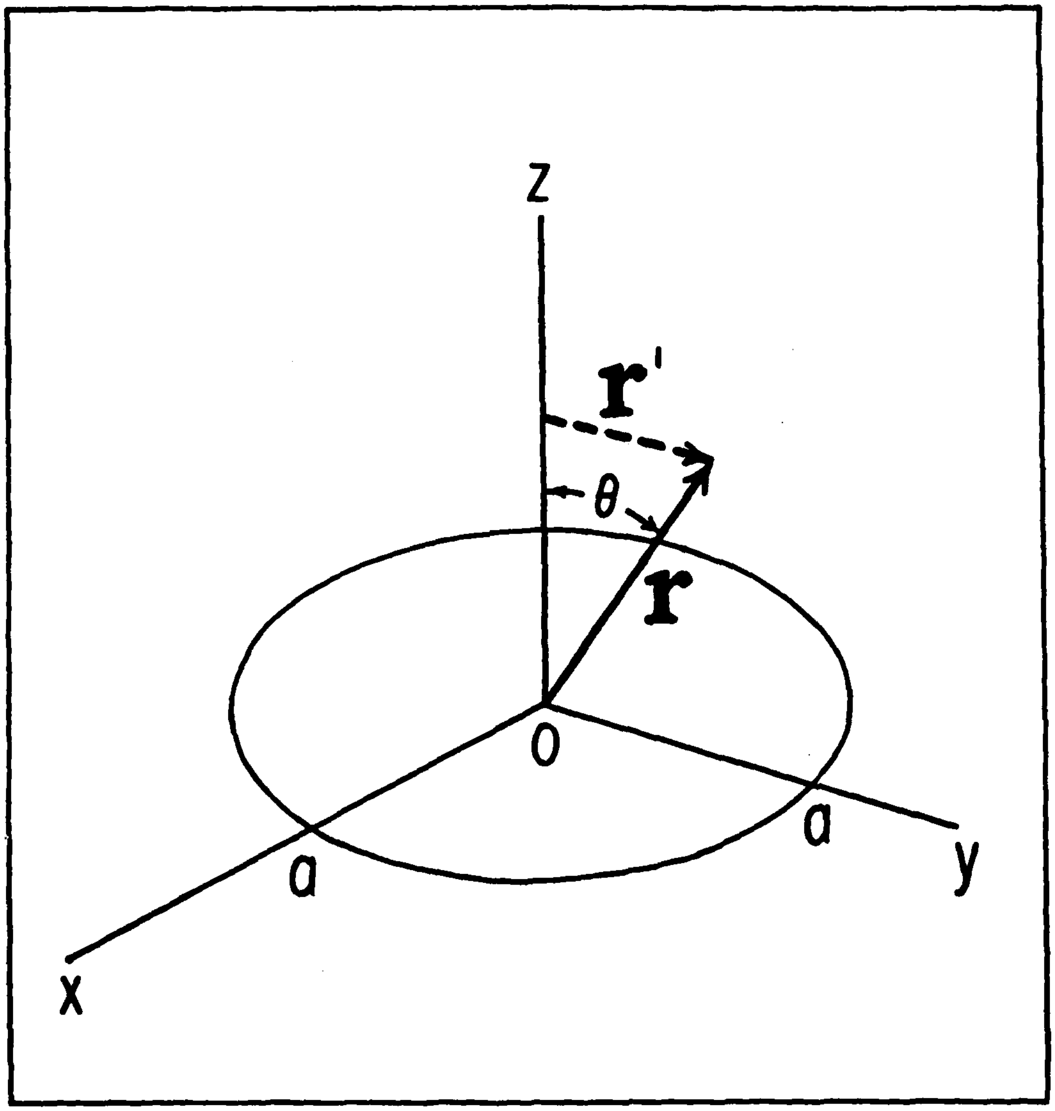
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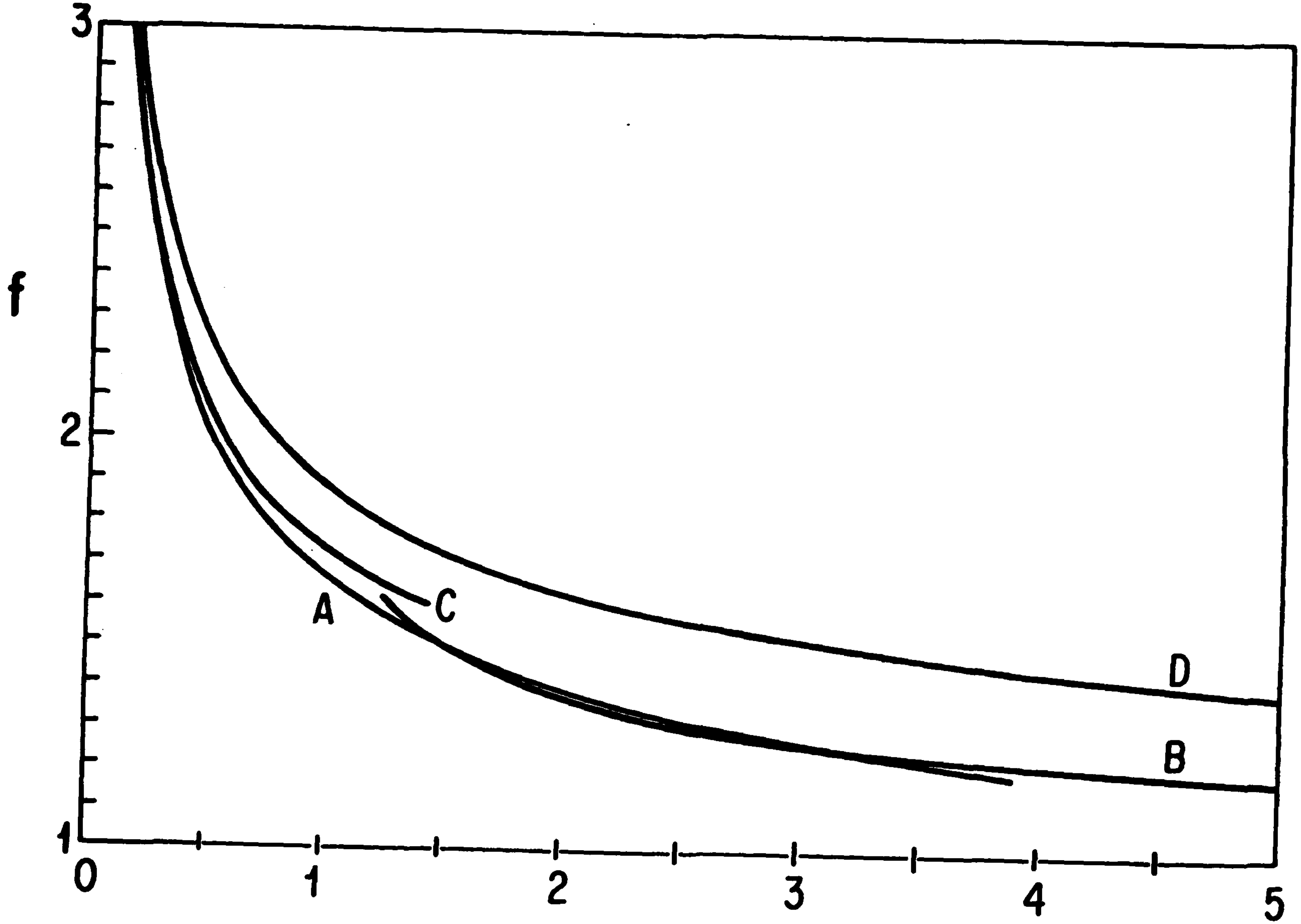
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